

# Theoretical studies on separation of CO<sub>2</sub> by single and blended aqueous alkanolamine solvents in flat sheet membrane contactor (FSMC)

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## Abstract

Absorption of carbon dioxide by different single and blended alkanolamine solvents were studied theoretically using flat sheet membrane contactor. The solvents considered for this study include aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) as well as aqueous blends MEA or DEA with AMP or MDEA. Simulation study shows that the absorption flux for CO<sub>2</sub> with aqueous solution of MEA was the highest among the single amines solvents studied. There is an increase in CO<sub>2</sub> absorption flux with the increase in the concentration of MEA or DEA in the blends of (MEA + MDEA), (DEA + MDEA) and (MEA + AMP). For the (DEA + AMP) system the flux of CO<sub>2</sub> is found to have a marginal effect with different blend compositions. The blends of (MEA + MDEA) and (MEA + AMP) are found comparatively suitable for the absorption of CO<sub>2</sub> among all the blends. The performance of flat sheet membrane contactor is found to be better than that of hollow fiber membrane contactor if only the absorption flux of CO<sub>2</sub> in the amine is considered. © 2008 Elsevier B.V. All rights reserved.

**Keywords:** Carbon dioxide; Absorption; Flat sheet membrane contactor; Alkanolamine

## 1. Introduction

Over the past few decades global expansion of industrial activities are increasing significantly the concentrations of some gases in the atmosphere, such as greenhouse gases (primarily CO<sub>2</sub>), which tend to warm the earth surface. CO<sub>2</sub> is emitted from fossil fuel, natural and refinery off gases and many other sources. CO<sub>2</sub> removal from different process streams is thus essential to prevent the danger of global warming. The alkanolamine-based processes have been used commercially for the removal of CO<sub>2</sub>. Conventional techniques such as column absorption for CO<sub>2</sub> are energy consuming and not easy to operate because of the frequent problems including flooding, foaming, channeling and entrainment. Micro-porous membrane contactors can overcome the major drawbacks of the conventional equipment when incorporated into the acid gas treating processes [1]. The membrane also provides much larger gas–liquid interfacial area than that of conventional contactors but suffers from the disadvantage of additional diffusional resistance through the gas filled membrane pores [2].

Though several researchers [3–18] reported the absorption of CO<sub>2</sub> in different single and blended alkanolamine solvents using conventional gas–liquid contactors, a few literatures only reported studies using membrane contactor. These studies have mainly concentrated on the hollow fiber membrane contactors [19–22]. Recently, we have reported a theoretical study [23] on the absorption of CO<sub>2</sub> in aqueous solutions of different single as well as blended alkanolamine solvents using hollow fiber membrane contactor (HFMC). A total of 10 wt.% alkanolamine was considered in all cases to compare the performance of different solvents using HFMC. Among the single amine solutions the aqueous solution of MEA was found the most suitable for the absorption of CO<sub>2</sub> if only the average flux of CO<sub>2</sub> in the amine is considered. For the absorption in the blends of (MEA + MDEA), (DEA + MDEA) and (MEA + AMP), the flux increased as the concentration of MEA or DEA increased in the blends. The absorption performance in the different blends of (DEA + AMP) was literally same. However, information regarding the removal of CO<sub>2</sub> using flat sheet membrane contactor is very much scarce. The main advantage of this contactor is that any type of membrane can be formed into flat sheet membrane module and the fabrication of flat sheet membrane is also easier compared to other membranes. The flux in flat sheet membrane is also higher than other membranes like hollow fiber and tubular membrane

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**Nomenclature**

$C$	concentration of components in liquid ( $\text{mol m}^{-3}$ )
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$J$	average absorption flux along the fiber length ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$J_{\text{local}}$	local absorption flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$k_b$	second order reaction rate constant for base b ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k_{\text{ext}}$	overall gas phase mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_g$	gas phase mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_m$	membrane phase mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_{-1}$	reverse first order reaction rate constant ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k_2$	second order forward reaction rate constant ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$L$	length of membrane (m)
$m$	distribution coefficient ( $\text{mol mol}^{-1}$ )
$M$	molar mass ( $\text{kg kmol}^{-1}$ )
$Q_L$	liquid flow rate ( $\text{cm}^3 \text{s}^{-1}$ )
$R_i$	rate of reaction ( $\text{mol m}^{-3} \text{s}^{-1}$ )
$T$	temperature (K)
$v_L$	average velocity of liquid ( $\text{m s}^{-1}$ )
$v_y$	velocity of liquid in y direction ( $\text{m s}^{-1}$ )
$v_z$	velocity of liquid in the z direction ( $\text{m s}^{-1}$ )
$W$	width between wall and membrane (m)
$y$	coordinate in transversal direction
$z$	coordinate in longitudinal direction

**Subscripts**

A	$\text{CO}_2$
B, C	alkanolamine
g	gas phase
i	interface, component

**Greek letter**

$\omega$	rate of absorption ( $\text{mol s}^{-1}$ )
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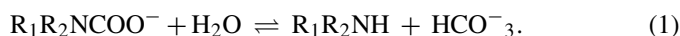
[24]. Wang et al. [25] have studied the absorption of  $\text{CO}_2$  into water using parallel-plate gas–liquid membrane contactor and to the best of our knowledge, detailed analysis on the performances of the flat sheet membrane contactor (FSMC), particularly for different single and blended amines, towards absorption of  $\text{CO}_2$  are not reported yet in the literature. This simulation work is an initial approach towards that direction which gives a preliminary idea regarding the absorption performance of different single and blended aqueous alkanolamine solvents using FSMC.

In the present work, we have developed a steady state mathematical model based on the fundamental conservation equation (component mass balance for the present case) applicable to flat sheet membrane contactor (FSMC) system. The model is simulated numerically to understand the local and average fluxes during absorption of  $\text{CO}_2$  in different single and blended aqueous alkanolamines. The alkanolamine solvent systems considered here are the aqueous

solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) as well as aqueous blends of (MEA + MDEA), (MEA + AMP), (DEA + MDEA) and (DEA + AMP). In this case we have considered a total of  $1000 \text{ mol m}^{-3}$  amine in all cases to compare the performance of different solvents more accurately in equimolar basis.

**2. Model development****2.1. Reaction mechanism of  $\text{CO}_2$  with amines**

The reaction of  $\text{CO}_2$  with primary and secondary amines is described by zwitterionic mechanism. The reaction mechanism and the reaction rates of  $\text{CO}_2$  with MEA and DEA are same as discussed in our recent publication [23]. However, for the reaction of  $\text{CO}_2$  with AMP we have assumed that the carbamate is hydrolyzed to form bicarbonate and it is quite reasonable because being a sterically hindered amine, the carbamate stability constant for AMP is very low [26].



So, the overall rate of reaction  $\text{CO}_2$  with AMP is expressed as

$$R_A = k_{2,\text{Amine}} C_A C_{\text{Amine}} \quad (2)$$

where A denotes  $\text{CO}_2$  and  $\text{R}_1$  and  $\text{R}_2$  are alkyl group. The reaction of  $\text{CO}_2$  with tertiary amine MDEA is discussed in our earlier publication [23] and the same is considered here.

For the reaction of  $\text{CO}_2$  with the blends of (MEA(B) + MDEA(C)), (MEA(C) + AMP(B)) and (DEA(B) + AMP(C)) the reaction rate can be expressed as

$$R_A = R_{A-B} + R_{A-C} \quad (3)$$

where

$$R_{A-B} = \frac{k_{2,B} C_A C_B}{1 + 1/((k_{\text{H}_2\text{O}})/(k_{-1})C_{\text{H}_2\text{O}}) + ((k_B)/(k_{-1})C_B) + ((k_C)/(k_{-1})C_C)} \quad (4)$$

and

$$R_{A-C} = k_{2,C} C_A C_C \quad (5)$$

Here B and C denote the amines in the blends. For the blends of (MEA(B) + MDEA(C)) and (DEA(B) + AMP(C)) [11,27] the reaction mechanism of  $\text{CO}_2$  with MEA or DEA involves the formation of zwitterion and then the deprotonation of the zwitterion by  $\text{H}_2\text{O}$  and the amines present in the solution. The reaction of  $\text{CO}_2$  with AMP or MDEA is same as already discussed for single amine. For the blends of (MEA(C) + AMP(B)) the reaction of  $\text{CO}_2$  with AMP was considered to be according to the zwitterionic mechanism whereas, an overall second order reaction rate is considered for the reaction of  $\text{CO}_2$  with MEA [7]. For the blends of (DEA(B) + MDEA(C)), zwitterionic mechanism is assumed for the reaction of  $\text{CO}_2$  with DEA. But, the contribution of MDEA in the deprotonation of zwitterion is neglected in

Table 1  
Rate expressions of amines

Aqueous amine solution	$R_B$ (mol m <sup>-3</sup> s <sup>-1</sup> )	$R_C$ (mol m <sup>-3</sup> s <sup>-1</sup> )
Single amines		
MEA(B) and DEA (B)	$\frac{k_{2,B} C_A C_B}{1 + 1/((k_{H_2O})/(k_{-1})C_{H_2O}) + ((k_B)/(k_{-1})C_B)}$	
MDEA (B) and AMP (B)	$k_{2,B} C_A C_B$	
Blended amines		
MEA (B) + MDEA (C), MEA (C) + AMP (B) and DEA (B) + AMP (C)	$\frac{k_{2,B} C_A C_B}{1 + 1/((k_{H_2O})/(k_{-1})C_{H_2O}) + ((k_B)/(k_{-1})C_B) + ((k_C)/(k_{-1})C_C)}$	$k_{2,C} C_A C_C$
DEA (B) + MDEA (C)	$\frac{k_{2,B} C_A C_B}{1 + 1/((k_{H_2O})/(k_{-1})C_{H_2O}) + ((k_B)/(k_{-1})C_B)}$	$k_{2,C} C_A C_C$

this case [6]. The reaction rates of amines for the absorption of CO<sub>2</sub> into single and blended aqueous alkanolamines are reported in Table 1. The kinetic constants for all the single amine and blended amine systems used for the simulation study are listed in Table 2.

## 2.2. Equations describing the diffusion-reaction process

The schematic diagram of the flat sheet membrane contactor (FSMC) considered for the present study is shown in Fig. 1. Liquid is flowing through one side of the membrane and the pores of the membrane are filled with gas flowing in another side of the membrane.  $L$  is the length of the contactor and  $W$  is the distance between the contactor wall and the membrane in the liquid side. Thus, for the liquid flowing side, the component mass balance equations can be written as:

$$v_z \frac{\partial C_i}{\partial Z} = D_A \frac{\partial^2 C_i}{\partial y^2} - R_i \quad (6)$$

where  $i$  represents components A, B and C. A denotes CO<sub>2</sub> and B and C denote alkanolamines for blended amine systems. For single amine solution only B denotes the amine. Eq. (6) is derived based on the following assumptions:

- (i) steady-state and isothermal operation;
- (ii) fully developed velocity profile along  $y$ -direction;
- (iii) negligible velocity component in  $y$ -direction,  $v_y$ ; and
- (iv) negligible axial dispersion along  $z$ -direction.

Table 2  
Kinetic parameters at 303 K used in simulation

Systems	$k_{2,B}$ (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$k_{2,B} k_{H_2O}/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$k_{2,B} k_B/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$k_{2,B} k_C/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$k_{2,C}$ (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Reference
MEA(B) + H <sub>2</sub> O	8.98	$1.16 \times 10^{-5}$	$2.41 \times 10^{-3}$	–	–	Liao and Li [11]
DEA(B) + H <sub>2</sub> O	4.36	$8.50 \times 10^{-6}$	$1.30 \times 10^{-3}$	–	–	Littel et al. [35]
AMP(B) + H <sub>2</sub> O	$7.39 \times 10^{-1}$	–	–	–	–	Saha et al. [36]
MDEA(B) + H <sub>2</sub> O	$8.40 \times 10^{-3}$	–	–	–	–	Ko and Li [28]
MEA(B) + MDEA (C) + H <sub>2</sub> O	8.98	$1.16 \times 10^{-5}$	$2.41 \times 10^{-3}$	$5.31 \times 10^{-4}$	$7.30 \times 10^{-3}$	Liao and Li [11]
MEA(C) + AMP (B) + H <sub>2</sub> O	1.26	$1.13 \times 10^{-7}$	$1.62 \times 10^{-3}$	$9.93 \times 10^{-4}$	4.72	Xiao et al. [7]
DEA(B) + MDEA (C) + H <sub>2</sub> O	4.36	$8.50 \times 10^{-6}$	$1.30 \times 10^{-3}$	–	$5.77 \times 10^{-3}$	Littel et al. [35] and Versteeg and van Swaij [37]
DEA(B) + AMP (C) + H <sub>2</sub> O	$2.05 \times 10^2$	$1.16 \times 10^{-266}$	$1.02 \times 10^{-2}$	$5.92 \times 10^{-6}$	$7.59 \times 10^{-1}$	Wang and Li [27]

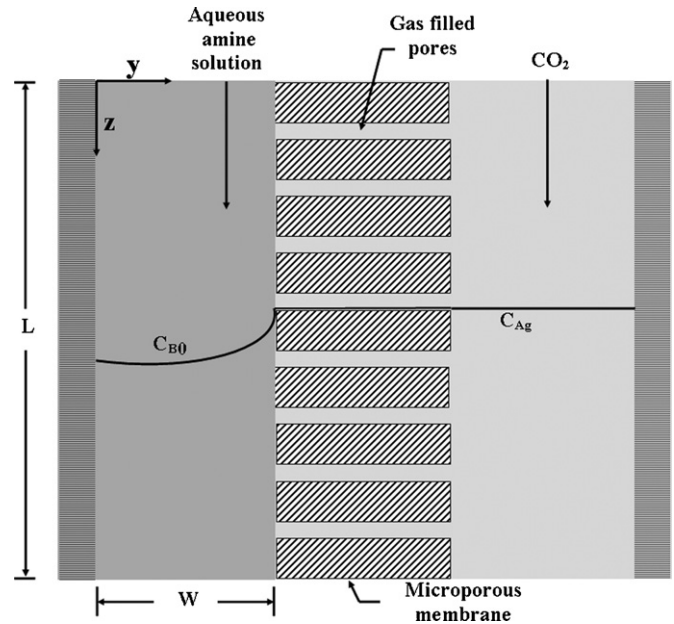


Fig. 1. Schematic drawing of absorption in hydrophobic flat sheet membrane.

In a laminar flow, a fully developed velocity profile can be described as:

$$v_z = 6v_L \left[ \left( \frac{y}{W} \right) - \left( \frac{y}{W} \right)^2 \right] \quad (7)$$

where  $v_L$  is the average velocity.

The boundary conditions in the axial and transversal directions respectively are:

$$\begin{aligned} \text{at } z = 0; \text{ for all } y; \quad C_A = 0, \quad C_B = C_{B0}, \\ C_C = C_{C0} \end{aligned} \quad (8)$$

and

$$\text{at } y = 0; \text{ for } z > 0; \quad \left( \frac{\partial C_i}{\partial y} \right) = 0. \quad (9)$$

For a non-volatile liquid phase component, the boundary condition at the gas–liquid interface is given by:

$$\text{at } y=W; \text{ for } z > 0; \quad \left( \frac{\partial C_B}{\partial y} \right) = 0, \quad \left( \frac{\partial C_C}{\partial y} \right) = 0. \quad (10)$$

At the gas–liquid interface, i.e. the membrane wall, mass transfer of the gas phase solute to the liquid phase occurs, which is described by:

$$D_A \left( \frac{\partial C_A}{\partial y} \right) = k_{\text{ext}}(C_{A,g} - C_{A,g,i}). \quad (11)$$

The Henry's law is applied to relate CO<sub>2</sub> interfacial concentrations in gas and liquid phase:

$$C_{A,i} = mC_{A,g,i}. \quad (12)$$

The overall gas phase mass transfer coefficient ( $k_{\text{ext}}$ ) is the sum of two resistances viz. the gas phase resistance ( $k_g$ ) and the membrane phase resistance ( $k_m$ ). In the present case,  $k_g$  is neglected considering the fact that the gas phase is well mixed in most practical operations and thus  $k_{\text{ext}} = k_m$ .

### 3. Method of solution

The set of partial differential equations along with the boundary conditions and the reaction rates were solved in MATLAB (The MathWorks, Natick, MA) using a built-in routine called *pdx4* to obtain the concentration profiles of CO<sub>2</sub> and different alkanolamines. The local absorption flux  $J_{A \text{ local}}$  of CO<sub>2</sub> along the length of the membrane was subsequently calculated using Fick's law. The average absorption flux  $J_A$  was obtained from the integration of the local fluxes along the length of the membrane:

$$J_A = \frac{1}{L} \int_0^L J_{A \text{ local}}(z) dz. \quad (13)$$

### 4. Results and discussion

The analysis is performed for the cases of pure CO<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> mixture. The CO<sub>2</sub> inlet concentration in case of CO<sub>2</sub>/N<sub>2</sub> mixture is taken as 20 vol.%. The gas phase concentration was assumed constant in the simulation. The total amine concentrations in all cases are taken as 1000 mol m<sup>-3</sup>. The length of the flat sheet membrane module considered in this study, is 0.2 m and the distance between the contactor wall and the membrane is 0.02 m. A liquid velocity of 0.1 m s<sup>-1</sup> is used in the simulation. The solubility of CO<sub>2</sub> in different single and blended

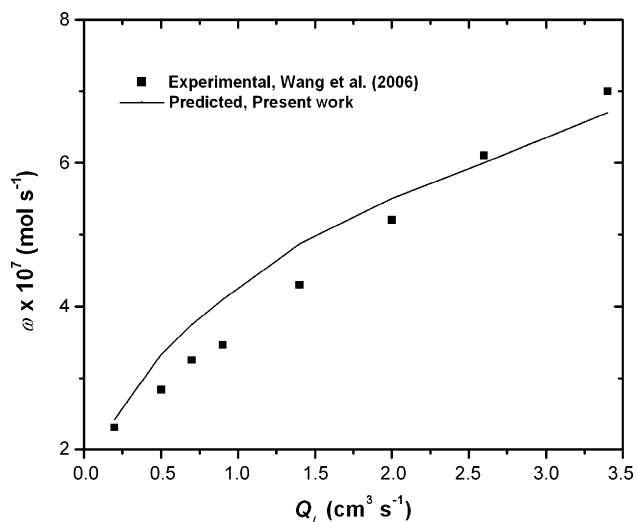


Fig. 2. Comparison of the CO<sub>2</sub> absorption rate in water.

amine solvents and the diffusivity coefficient of CO<sub>2</sub> and different alkanolamines were taken from the literature [28–34]. For the modeling of absorption of CO<sub>2</sub> in different aqueous alkanolamine solutions, we have taken the value of  $k_{\text{ext}}$  as 100 m s<sup>-1</sup> [23] during the simulation studies, which is a much higher value, to take care of the fact that the gas phase resistance is negligible and the efficiency of the membrane for different processes do not influence the fluxes obtained in the later part of the study.

Since to the best of our knowledge, there is no literature available regarding the absorption of CO<sub>2</sub> in alkanolamine solvents using flat sheet membrane contactor (FSMC), to validate the model and the numerical scheme, our simulation result for the physical absorption of 20% CO<sub>2</sub> in water using FSMC is compared with the experimental results reported by Wang et al. [25] (Fig. 2). The membrane geometry and operating parameters used in the validation are the same as those used by Wang et al. [25]. The value of  $k_{\text{ext}}$  is taken as 100 m s<sup>-1</sup>. As shown in Fig. 2, the present simulation result agrees well with the literature data of Wang et al. [25], the average deviation being about 10%. It is worth mentioning here that while studying the effect of  $k_{\text{ext}}$  on the CO<sub>2</sub> absorption flux in water for two different liquid flow rates, it was found that much lower values of  $k_{\text{ext}}$ , indicative of significant gas phase mass-transfer resistance, has distinct influence on the CO<sub>2</sub> absorption flux. The simulated flux with significantly lower value of  $k_{\text{ext}}$  predicts the experimental results of Wang et al. [25] better. This is not addressed further since we have neglected the gas phase resistance in the present work with the substantially high value of  $k_{\text{ext}} = 100 \text{ m s}^{-1}$  and found the simulation prediction within tolerable limit after compromising with the complexity and reality of the mathematical model.

#### 4.1. CO<sub>2</sub> absorption with single amine solvent

CO<sub>2</sub> absorption performances of different single amines are analyzed in terms of local flux of CO<sub>2</sub> along the length of the FSMC, the liquid phase CO<sub>2</sub> and amine concentration profiles. It can be observed from Fig. 3 for both 20% and pure CO<sub>2</sub> that the variation of local flux initially is a strong and decreasing

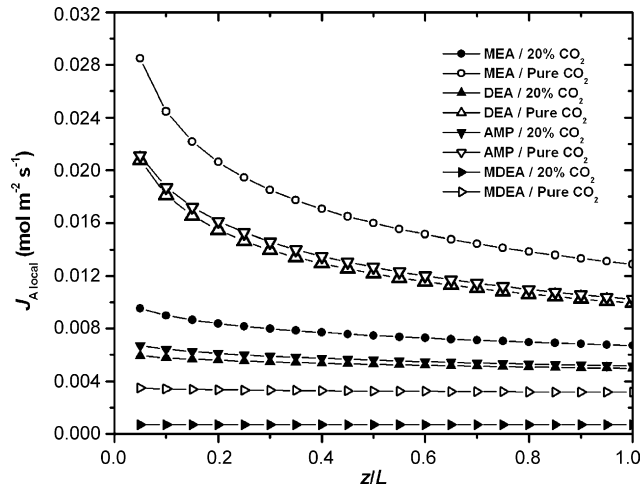


Fig. 3. Local  $\text{CO}_2$  absorption flux for 20% and pure  $\text{CO}_2$  in single amine solution over the membrane length.

and also later is weak but decreasing function of the length of the membrane. This decrease is quite sharp particularly for the cases of MEA, AMP and DEA having high reaction rate for  $\text{CO}_2$ . The sharpness of the decreasing trend gradually decreases with the amines having lower reaction rates. Similar observation was also observed in our previous study [23] using hollow fiber membrane contactor (membrane length is 0.2 m and fiber radius is  $2 \times 10^{-4}$  m). However, irrespective of the amine used, the average flux for the absorption of 20%  $\text{CO}_2$  is about 50% of that for the absorption of pure  $\text{CO}_2$ . There is no significant variation in the flux for the case of MDEA with 20%  $\text{CO}_2$  due to very low reaction rate compared to the others. Fig. 3 also clearly depicts the fact that the aqueous solution of MEA has the highest  $\text{CO}_2$  absorption flux followed by AMP, DEA and MDEA in sequence, which is again justified from the reaction kinetics of amines with  $\text{CO}_2$  reported in Table 2. Further, more amine is consumed due to continuous supply of  $\text{CO}_2$  with increase in the membrane length resulting in drop in amine concentration, which in turn leads to drop in  $\text{CO}_2$  flux as the reaction rate is a function of amine concentration. This is particularly so as in the present study  $\text{CO}_2$  concentration in the gas phase at the gas–liquid interface is

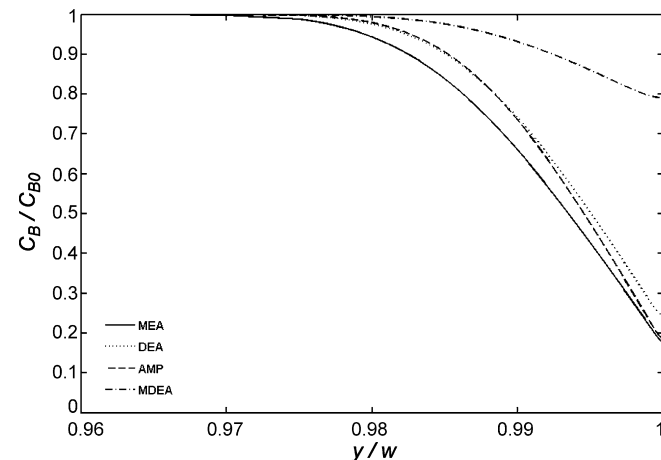


Fig. 4. Transversal concentration profile of amine for the absorption of 20%  $\text{CO}_2$  in the single amine solution at the liquid exit of the membrane.

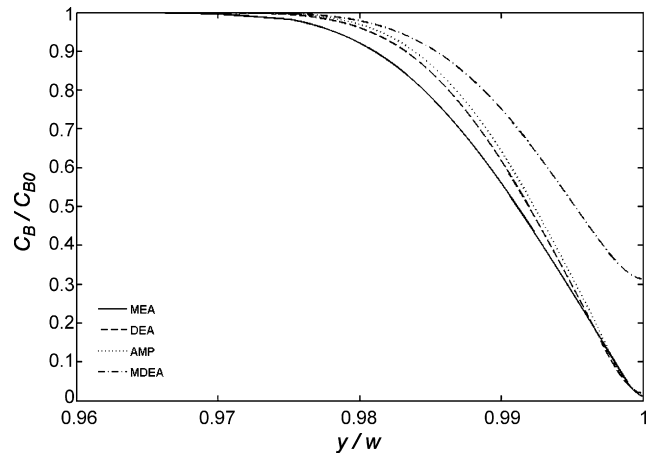


Fig. 5. Transversal concentration profile of amine for the absorption of pure  $\text{CO}_2$  in the single amine solution at the liquid exit of the membrane.

assumed constant and the reaction rate is the dominating factor over other transport and physico-chemical properties.

Figs. 4 and 5 describe the concentration profiles of four alkanolamines in liquid phase along the width of the FSMC for the absorption of 20% and pure  $\text{CO}_2$ , respectively. In both cases there are significant drops in concentrations for all the amines used. Depletion of MEA is the highest due to the highest reaction rate of MEA with  $\text{CO}_2$  than that of DEA, AMP and MDEA. Depletion of MDEA is the least because of its low reaction rate compared to other amines. The above behavior is also reflected in Figs. 6 and 7 where the concentration of unreacted  $\text{CO}_2$  is the least in MEA and the highest in MDEA for both the absorption of 20% and pure  $\text{CO}_2$ . So, from the above discussion it can be concluded that,  $\text{CO}_2$  absorption flux in amines follows the sequence  $\text{MEA} > \text{AMP} > \text{DEA} > \text{MDEA}$  irrespective of the concentration of  $\text{CO}_2$  in the gas phase.

#### 4.2. $\text{CO}_2$ absorption into blended amine

The performance of absorption of 20% and pure carbon dioxide into aqueous blends of (MEA + MDEA), (MEA + AMP), (DEA + MDEA) and (DEA + AMP) is analyzed in terms of aver-

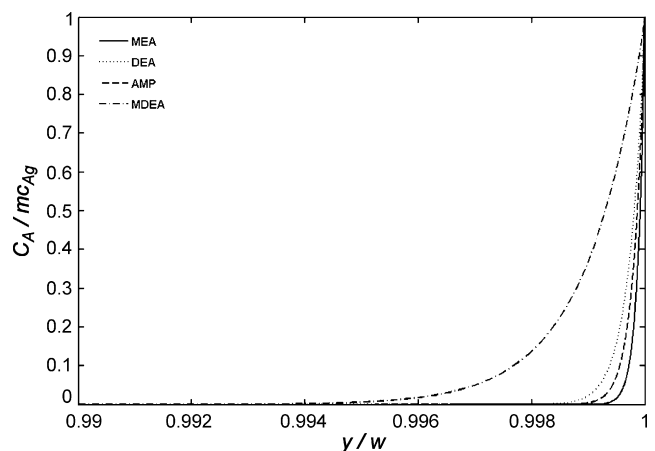


Fig. 6. Transversal concentration profile of  $\text{CO}_2$  for the absorption of 20%  $\text{CO}_2$  in the single amine solution at the liquid exit of the membrane.

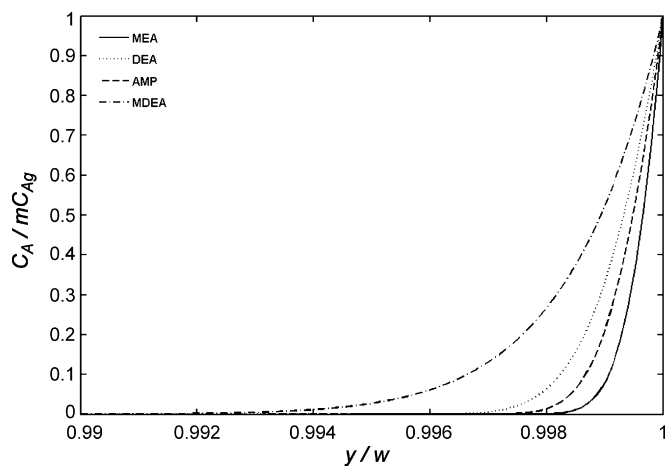


Fig. 7. Transversal concentration profile of CO<sub>2</sub> for the absorption of pure CO<sub>2</sub> in the single amine solution at the liquid exit of the membrane.

age flux of carbon dioxide over the membrane length, and the liquid phase concentration profile of CO<sub>2</sub> and the alkanolamines along the width of the FSMC. The concentrations of the amines were varied from 0 to 1000 mol m<sup>-3</sup> (maintaining the total amine concentration as 1000 mol m<sup>-3</sup> in the blend) to find the effects on CO<sub>2</sub> absorption.

Fig. 8 shows the average CO<sub>2</sub> absorption flux in different aqueous alkanolamine blends. Obviously, because of more driving force the absorption of pure CO<sub>2</sub> is much higher than that of 20% CO<sub>2</sub>. It was observed from this figure that for (MEA + AMP) and (MEA + MDEA) systems, the CO<sub>2</sub> absorption flux increased sharply with increase in MEA concentration in the blend. This is again due to much higher reaction rate of MEA for CO<sub>2</sub> than that of MDEA or AMP. For (DEA + MDEA) system, higher DEA concentration gives higher flux due to its relatively higher reaction rate compared to MDEA. AMP has slightly faster rate of absorption compared to DEA. Increasing concentration of DEA means that the AMP concentration in the blend is reduced and DEA even with higher concentration, its absorption rate is still lower compared to the AMP at the corre-

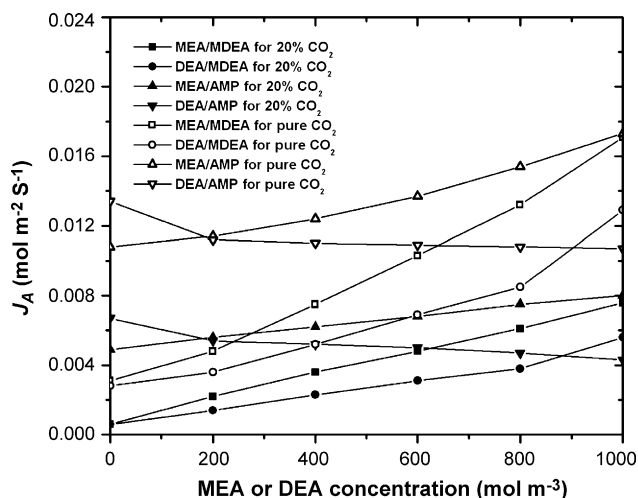


Fig. 8. Average CO<sub>2</sub> absorption flux over the membrane length as a function of amine blend composition.

sponding concentration. So, for the (DEA + AMP) systems the absorption flux decreases marginally with the increase in the concentration of DEA in the blend. This suggests that DEA is not suitable solvent in combination with AMP.

As shown in Fig. 8, the average absorption flux for pure CO<sub>2</sub> increased from 0.0048 mol m<sup>-2</sup> s<sup>-1</sup> for (200 mol m<sup>-3</sup> MEA + 800 mol m<sup>-3</sup> MDEA) to 0.0132 mol m<sup>-2</sup> s<sup>-1</sup> for (800 mol m<sup>-3</sup> MEA + 200 mol m<sup>-3</sup> MDEA) blend and becomes almost equal to the flux in 1000 mol m<sup>-3</sup> MEA, whereas the flux for pure CO<sub>2</sub> increased from 0.0036 mol m<sup>-2</sup> s<sup>-1</sup> for (200 mol m<sup>-3</sup> DEA + 800 mol m<sup>-3</sup> MDEA) to 0.0085 mol m<sup>-2</sup> s<sup>-1</sup> for (800 mol m<sup>-3</sup> DEA + 200 mol m<sup>-3</sup> MDEA) blend. The average absorption flux for pure CO<sub>2</sub> increased from 0.0114 to 0.0154 mol m<sup>-2</sup> s<sup>-1</sup> for (200 mol m<sup>-3</sup> MEA + 800 mol m<sup>-3</sup> AMP) blend to (800 mol m<sup>-3</sup> MEA + 200 mol m<sup>-3</sup> AMP) blend. According to Fig. 8, there are deviations between the average absorption fluxes of CO<sub>2</sub> into aqueous single amine solutions when we considered the reaction kinetics of CO<sub>2</sub> in their blends. These deviations may be due to the different experimental conditions and procedure followed by different authors. Particularly, for the absorption of CO<sub>2</sub> into aqueous solutions of (0 mol m<sup>-3</sup> MEA + 1000 mol m<sup>-3</sup> AMP) and that of into (0 mol m<sup>-3</sup> DEA + 1000 mol m<sup>-3</sup> AMP), this deviation is quite significant. This is due to the different reaction mechanism for AMP assumed in those two different blends. For the blends of (MEA + AMP) the reaction of CO<sub>2</sub> with AMP is assumed according to zwitterionic mechanism [7] whereas, an overall second order reaction rate is assumed in case of the blends of (DEA + AMP) for the reaction of CO<sub>2</sub> with AMP [27]. It can further be noticed from Fig. 8 that when the concentration of MEA or DEA is lower in the blends of (MEA + AMP) or (DEA + AMP), respectively, the flux of CO<sub>2</sub> is greater than that in the blends of (MEA + MDEA) because the reaction rate of CO<sub>2</sub> with AMP is much higher than that with MDEA. Further, the above said difference in flux reduces gradually as the concentration of MEA or DEA increase in the blends. At higher concentrations of MEA or DEA in the blends, the performance of (MEA + MDEA) blends is better than that of (DEA + AMP) blends and almost becomes comparable to that of (MEA + AMP) blends, if the average absorption flux of CO<sub>2</sub> is only considered. On the other hand, MDEA has better regeneration characteristics than other amines studied, as MDEA is having low heat of reaction with CO<sub>2</sub>, which leads to lower energy requirement for regeneration. So the (MEA + MDEA) is better for the absorption of CO<sub>2</sub> from the regeneration point of view the solvents. Thus, from the above discussion it can be concluded that either of (MEA + MDEA) or (MEA + AMP) blends can preferably be used for the absorption of CO<sub>2</sub> using FSMC. Of course, the better of the two can be more distinctly predicted after carrying out regeneration study of these solvents.

The concentration profiles of CO<sub>2</sub> for the absorption of 20% and pure CO<sub>2</sub> absorption in aqueous blends of (MEA + MDEA) are described in Figs. 9 and 10. In all the cases the liquid phase carbon dioxide concentration profile with width at the liquid exit shifted to the right side as the concentration of MEA in

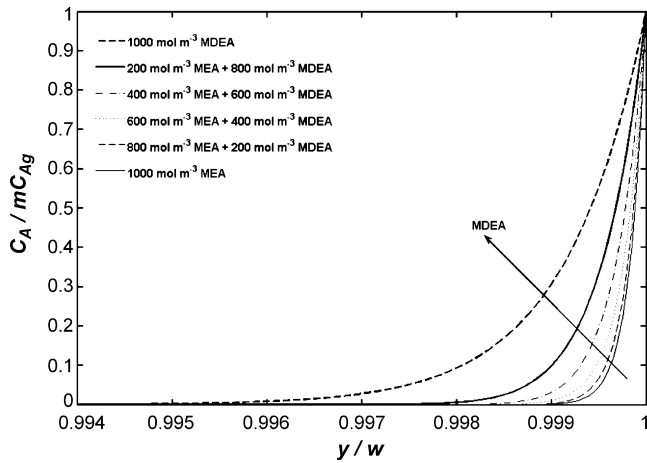


Fig. 9. Transversal concentration profile of 20% CO<sub>2</sub> in the (MEA + MDEA) blended amine solution at the liquid exit of the membrane.

the blend increased. The difference is gradually decreased with the increase in MEA concentration because of higher reaction rate of MEA (Figs. 9 and 10). Similar behavior for the blends of (MEA + AMP) was obtained (not reported here) with closer concentration profiles of CO<sub>2</sub> as the reaction rates of CO<sub>2</sub> with MEA and AMP are closer to each other.

#### 4.3. Comparison of the performance of FSMC and HFMC

To compare the performance of FSMC and HFMC, the absorption of pure CO<sub>2</sub> was theoretically analyzed using both the membrane contactors. The mass balance equations regarding the diffusion-reaction process in the HFMC and the module properties are same as discussed in our earlier publication [23]. Figs. 11 and 12 show the local absorption flux along the length of membrane of pure and 20% CO<sub>2</sub> in aqueous solutions of MEA, DEA, AMP and MDEA using HFMC and FSMC. The trend of fluxes is same for both the contactors, i.e., the flux is more for amines having high reaction rate towards CO<sub>2</sub> (MEA, DEA and AMP in this case) and the variation of the membrane length (fiber length for HFMC) does not have much impact on the CO<sub>2</sub>

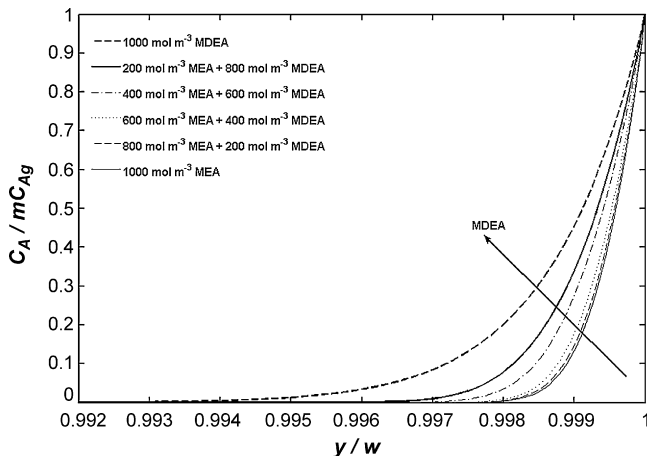


Fig. 10. Transversal concentration profile of pure CO<sub>2</sub> in the (MEA + MDEA) blended amine solution at the liquid exit of the membrane.

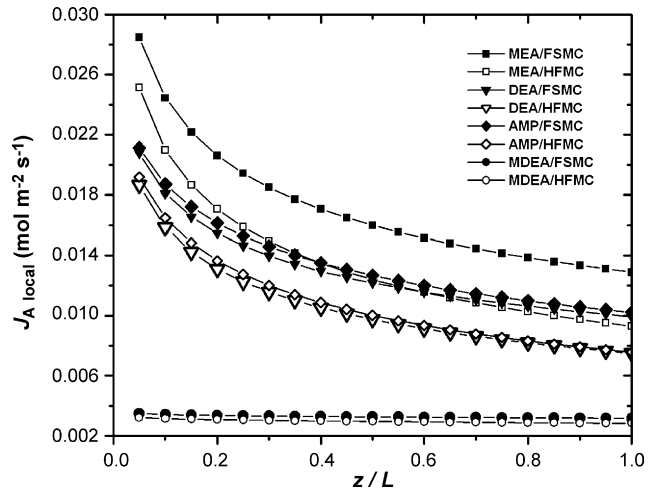


Fig. 11. Local CO<sub>2</sub> absorption flux for pure CO<sub>2</sub> in single amine solution over the membrane length of FSMC and HFMC.

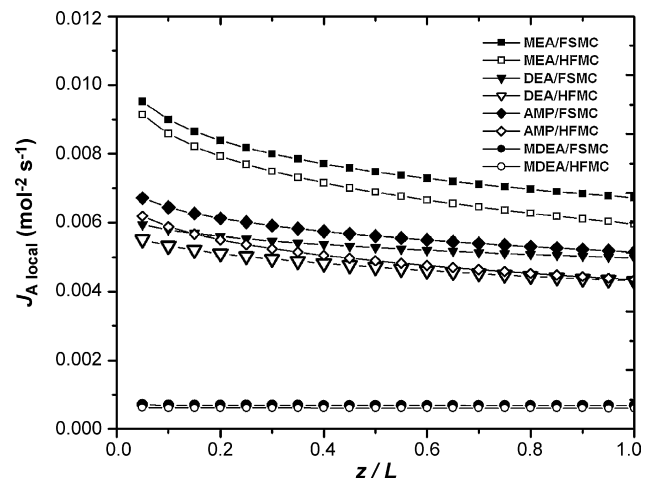


Fig. 12. Local CO<sub>2</sub> absorption flux for 20% CO<sub>2</sub> in single amine solution over the membrane length of FSMC and HFMC.

absorption in MDEA solution under simulated conditions due to its smaller reaction rate constant. But, in all cases the flux is greater for the absorption using FSMC. The differences between the average absorption fluxes using HFMC and FSMC for the absorption of 20% CO<sub>2</sub> are lower compared to those obtained for the absorption of pure CO<sub>2</sub>. The average absorption fluxes in those amines for HFMC and FSMC are listed in Table 3. So, if only absorption flux is considered, FSMC performs better but

Table 3  
Average absorption flux for the absorption of CO<sub>2</sub> using FSMC and HFMC

Solvent (amine concentration 1000 mol m <sup>-3</sup> )	$J$ (mol m <sup>-2</sup> s <sup>-1</sup> )			
	Pure CO <sub>2</sub>		20% CO <sub>2</sub>	
	FSMC	HFMC	FSMC	HFMC
MEA + H <sub>2</sub> O	0.0171	0.0135	0.0076	0.0070
AMP + H <sub>2</sub> O	0.0134	0.0108	0.0056	0.0049
DEA + H <sub>2</sub> O	0.0129	0.0105	0.0053	0.0047
MDEA + H <sub>2</sub> O	0.0033	0.0030	0.0007	0.0006

the choice of the more suitable membrane module type for a particular membrane separation must depend on number of factors. The factors are module geometry and membrane properties like membrane material, pore size and porosity, specific surface area, etc. and different operating parameters like gas and liquid flow rates, initial solvent and gas phase CO<sub>2</sub> concentration, pressure drop considerations, etc. Hollow fiber modules are significantly cheaper, per square meter of membrane, than flat sheet modules. Hence, the better performance between FSMC and HFMC can be more accurately predicted after examining the influence of different parameters as well as making a techno-economic analysis.

## 5. Conclusion

From the theoretical analysis of the absorption of CO<sub>2</sub> in different alkanolamine solvents it can be concluded that the aqueous solution of MEA is the most suitable for the absorption of CO<sub>2</sub> among the single amine solutions, if only the average flux of CO<sub>2</sub> in the amine is considered. For the absorption in the blends of (MEA + MDEA), (DEA + MDEA) and (MEA + AMP), the flux increases as the concentration of MEA or DEA increases in the blends. The absorption performance of the different compositions of (DEA + AMP) blend is literally same. At lower concentrations of MEA or DEA in the blends of (MEA + MDEA), (DEA + AMP) and (MEA + AMP), the flux of CO<sub>2</sub> is greater in the last two blends whereas at higher concentrations of MEA or DEA the flux in the blends of (MEA + MDEA) is higher than that in the blends of (DEA + AMP) and flux becomes comparable to that with the blends of (MEA + AMP). But, the ultimate choice of the solvent for the absorption of CO<sub>2</sub> depends upon the detailed analysis about the regeneration characteristics of the solvents. The CO<sub>2</sub> absorption flux in FSMC is higher than that in HFMC for all high to low reacting alkanolamines. A further techno-economical analysis is required to select better contactor between FSMC and HFMC for CO<sub>2</sub> separation.

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## References

- [1] A. Gabelman, S.-T. Hwang, Hollow fiber membrane contactors, *J. Membr. Sci.* 159 (1999) 61.
- [2] K.K. Sirkar, Other new membrane processes, in: W.S. Winstone Ho, K.K. Sirkar (Eds.), *Membrane Handbook*, Van Nostrand Reinhold, New York, 1992.
- [3] B.P. Mandal, A.K. Biswas, S.S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine, *Chem. Eng. Sci.* 58 (2003) 4137.
- [4] B.P. Mandal, M. Guha, A.K. Biswas, S.S. Bandyopadhyay, Removal of carbon dioxide by absorption in mixed amines: modelling of absorption in aqueous MDEA/MEA and AMP/MEA solutions, *Chem. Eng. Sci.* 56 (2001) 6217.
- [5] B.P. Mandal, S.S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine, *Chem. Eng. Sci.* 61 (2006) 5440.
- [6] E.B. Rinker, S.S. Ashour, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of diethanolamine and *N*-methyldiethanolamine, *Ind. Eng. Chem. Res.* 39 (2000) 4346.
- [7] J. Xiao, C.W. Li, M.H. Li, Kinetics of absorption of carbon dioxide into aqueous solutions of 2-amino-2-methyl-1-propanol + monoethanolamine, *Chem. Eng. Sci.* 55 (2000) 161.
- [8] P.M.M. Blauwhoff, G.F. Versteeg, W.P.M. van Swaaij, A study on the reaction between CO<sub>2</sub> and alkanolamines in aqueous solutions, *Chem. Eng. Sci.* 39 (1984) 207.
- [9] S. Xu, Y.W. Wang, F.D. Otto, A.E. Mather, Kinetics of the reaction of CO<sub>2</sub> with 2-amino-2-methyl-1-propanol solutions, *Chem. Eng. Sci.* 51 (1996) 841.
- [10] D.A. Glasscock, Modeling and Experimental Study of Carbon Dioxide Absorption in Aqueous Alkanolamines, Ph.D. Dissertation, The University of Texas at Austin, 1990.
- [11] C.H. Liao, M.H. Li, Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + *N*-methyldiethanolamine, *Chem. Eng. Sci.* 57 (2002) 4569.
- [12] D.P. Hagewiesche, S.S. Ashour, H.A. Al-Ghawas, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of monoethanolamine and *N*-methyldiethanolamine, *Chem. Eng. Sci.* 50 (1995) 1071.
- [13] D.A. Glasscock, J.E. Critchfield, G.T. Rochelle, CO<sub>2</sub> absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine, *Chem. Eng. Sci.* 46 (1991) 2829.
- [14] A. Aroonwilas, A. Chakma, P. Tontiwachwuthikul, A. Veawab, Mathematical modelling of mass-transfer and hydrodynamics in CO<sub>2</sub> absorbers packed with structured packings, *Chem. Eng. Sci.* 58 (2003) 4037.
- [15] J. Gabrielsen, H.F. Svendsen, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Experimental validation of a rate-based model for CO<sub>2</sub> capture using an AMP solution, *Chem. Eng. Sci.* 62 (2007) 2397.
- [16] J. Gabrielsen, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Modeling of CO<sub>2</sub> absorber using an AMP solution, *AIChE J.* 52 (2006) 3443.
- [17] A. Aboudheir, P. Tontiwachwuthikul, R. Idem, Rigorous model for predicting the behavior of CO<sub>2</sub> absorption into AMP in packed-bed absorption columns, *Ind. Eng. Chem. Res.* 45 (2006) 2553.
- [18] F. Camacho, S. Sanchez, R. Pacheco, A. Sanchez, M.D. La Rubia, Thermal effects of CO<sub>2</sub> absorption in aqueous solutions of 2-amino-2-methyl-1-propanol, *AIChE J.* 51 (2005) 2769.
- [19] Y. Lee, R.D. Noble, B.-Y. Yeom, Y.-I. Park, K.-H. Lee, Analysis of CO<sub>2</sub> removal by hollow fiber membrane contactors, *J. Membr. Sci.* 194 (2001) 57.
- [20] R. Wang, D.F. Li, D.T. Liang, Modelling of CO<sub>2</sub> capture by three typical amine solutions in hollow fiber membrane contactors, *Chem. Eng. Process.* 43 (2004) 849.
- [21] H.-Y. Zhang, R. Wang, D.T. Liang, J.H. Tay, Modeling and experimental study of CO<sub>2</sub> absorption in a hollow fiber membrane contactor, *J. Membr. Sci.* 279 (2006) 301.
- [22] Y. Gong, Z. Wang, S. Wang, Experiments and simulation of CO<sub>2</sub> removal by mixed amines in a hollow fiber membrane module, *Chem. Eng. Process.* 45 (2006) 652.
- [23] S. Paul, A.K. Ghoshal, B. Mandal, Removal of CO<sub>2</sub> by single and blended aqueous alkanolamine solvents in hollow-fiber membrane contactor: modeling and simulation, *Ind. Eng. Chem. Res.* 46 (2007) 2576.
- [24] W.B. Richard, *Membrane Technology and Applications*, John Wiley & Sons Ltd., England, 2004.
- [25] W.P. Wang, H.T. Lin, C.D. Ho, An analytical study of laminar co-current flow gas absorption through a parallel-plate gas-liquid membrane contactor, *Ind. Eng. Chem. Res.* 278 (2006) 181.
- [26] G. Sartori, W.S. Ho, D.W. Savage, G.R. Chludzinski, S. Wiechert, Sterically hindered amines for acid-gas absorption, *Sep. Purif. Methods* 16 (1987) 171.
- [27] H.M. Wang, M.H. Li, Kinetics of absorption of carbon dioxide into aqueous solutions of 2-amino-2-methyl-1-propanol + diethanolamine, *J. Chem. Eng. Jpn.* 37 (2004) 267.
- [28] J.J. Ko, M.H. Li, Kinetics of absorption of carbon dioxide into solutions of *N*-methyldiethanolamine + water, *Chem. Eng. Sci.* 55 (2000) 4139.



- [29] T.C. Tsai, J.J. Ko, H.M. Wang, C.Y. Lin, M.H. Li, Solubility of nitrous oxide in alkanolamine aqueous solutions, *J. Chem. Eng. Data* 45 (2000) 341.
- [30] J.J. Ko, T.C. Tsai, C.Y. Lin, H.M. Wang, M.H. Li, Diffusivity of nitrous oxide in alkanolamine aqueous solutions, *J. Chem. Eng. Data* 46 (2001) 160.
- [31] E.D. Snijder, M.J.M. te Riele, G.F. Versteeg, W.P.M. van Swaaij, Diffusion coefficients of several alkanolamine solutions, *J. Chem. Eng. Data* 38 (1993) 475.
- [32] C.L. Chang, T.I. Lin, M.H. Li, Mutual diffusion coefficients of some aqueous alkanolamine solutions, *J. Chem. Eng. Data* 50 (2005) 77.
- [33] B.P. Mandal, M. Kundu, N.U. Padhiyar, S.S. Bandyopadhyay, Physical solubility and diffusivity of  $N_2O$  and  $CO_2$  into aqueous solutions of (2-amino-2-methyl-1-propanol + diethanolamine) and (*N*-methyldiethanolamine + diethanolamine), *J. Chem. Eng. Data* 49 (2004) 264.
- [34] B.P. Mandal, M. Kundu, S.S. Bandyopadhyay, Physical solubility and diffusivity of  $N_2O$  and  $CO_2$  into aqueous solutions of (2-amino-2-methyl-1-propanol + monoethanolamine) and (*N*-methyldiethanolamine + monoethanolamine), *J. Chem. Eng. Data* 50 (2005) 352.
- [35] R.J. Littel, G.F. Versteeg, W.P.M. van Swaaij, Kinetics of  $CO_2$  with primary and secondary amines in aqueous solutions. Part II. Influence of temperature on zwitterion formation and deprotonation rates, *Chem. Eng. Sci.* 47 (1992) 2037.
- [36] A.K. Saha, S.S. Bandyopadhyay, A.K. Biswas, Solubility and diffusivity of nitrous oxide and carbon dioxide in aqueous solutions of 2-amino-2-methyl-1-propanol, *J. Chem. Eng. Data* 38 (1993) 78.
- [37] G.F. Versteeg, W.P.M. van Swaaij, On the kinetics between  $CO_2$  and alkanolamines both in aqueous non-aqueous solutions. Part II. Tertiary amines, *Chem. Eng. Sci.* 43 (1988) 587.